Chapter 20
Electrochemistry

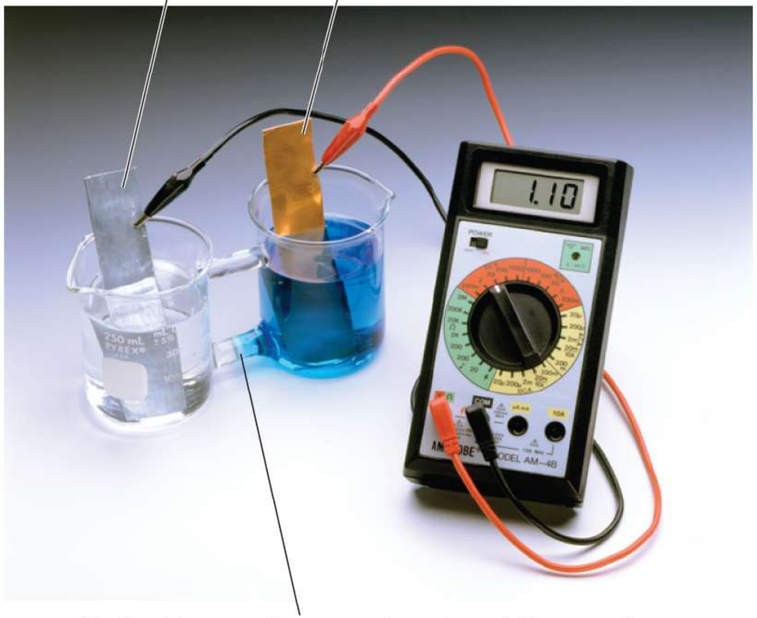
Electrochemistry

Electrochemistry is the study of the relationships between electricity and chemical reactions. It includes the study of both spontaneous and nonspontaneous processes.

20.3 Voltaic Cells

Voltaic Cells

- In spontaneous redox reactions, electrons are transferred and energy is released.
- That energy can do work if the electrons flow through an external device.
- This is a **voltaic cell**.

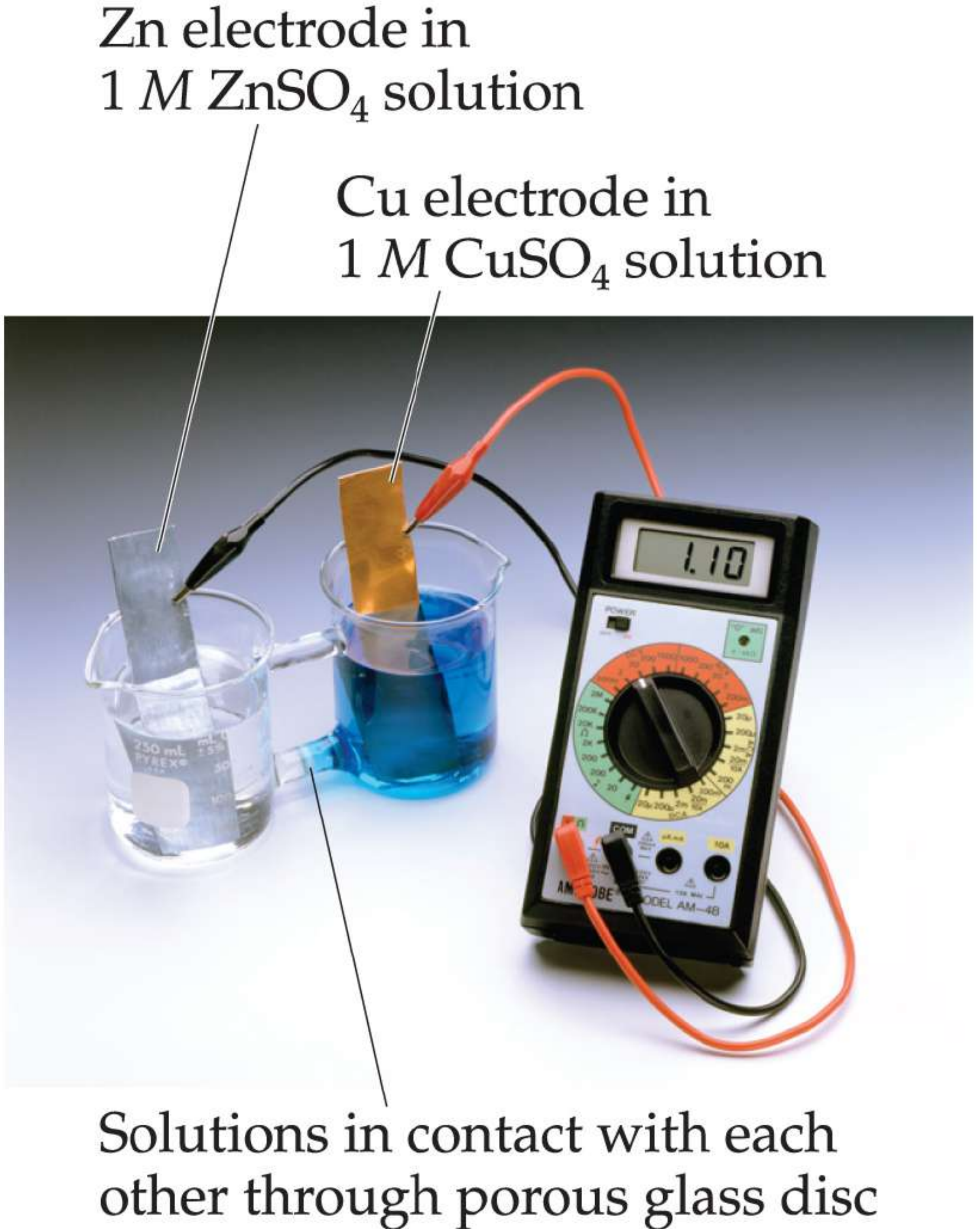


Zn electrode in
1 *M* $ZnSO_4$ solution

Cu electrode in
1 *M* $CuSO_4$ solution

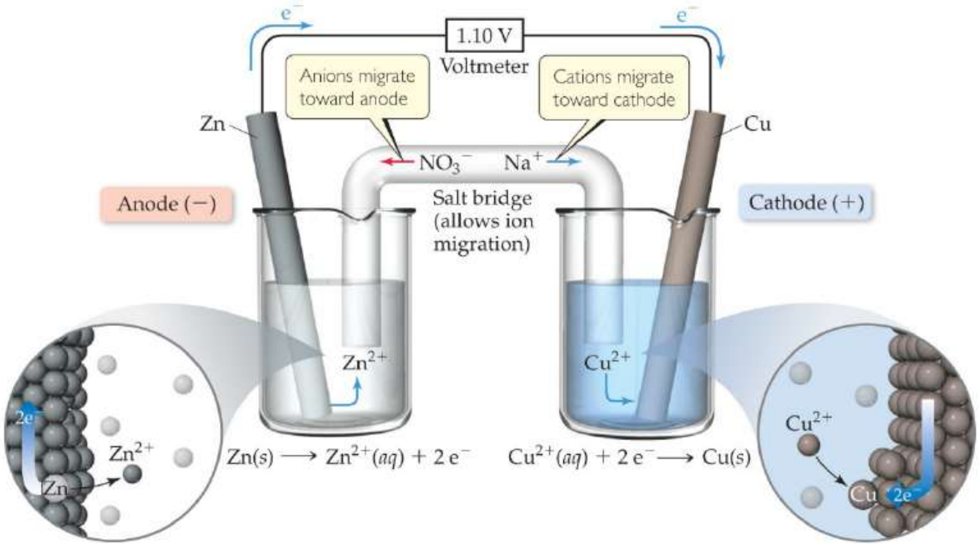
Solutions in contact with each
other through porous glass disc

- Which metal, Cu or Zn, is oxidized in this voltaic cell?

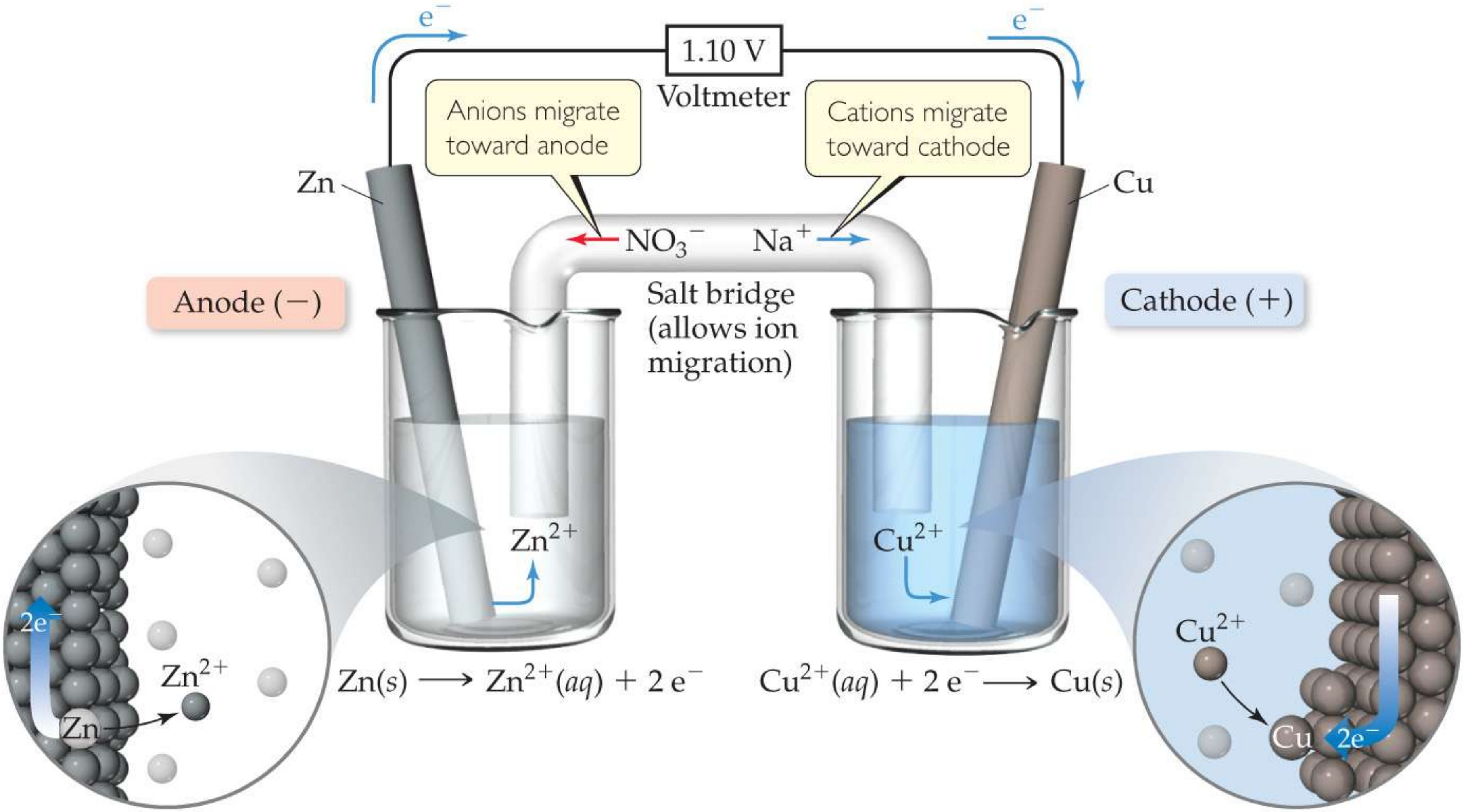


Voltaic Cells

- The oxidation occurs at the **anode**.
- The reduction occurs at the **cathode**.
- When electrons flow, charges aren’t balanced. So, a salt bridge, usually a U-shaped tube that contains a salt/agar solution, is used to keep the charges balanced.

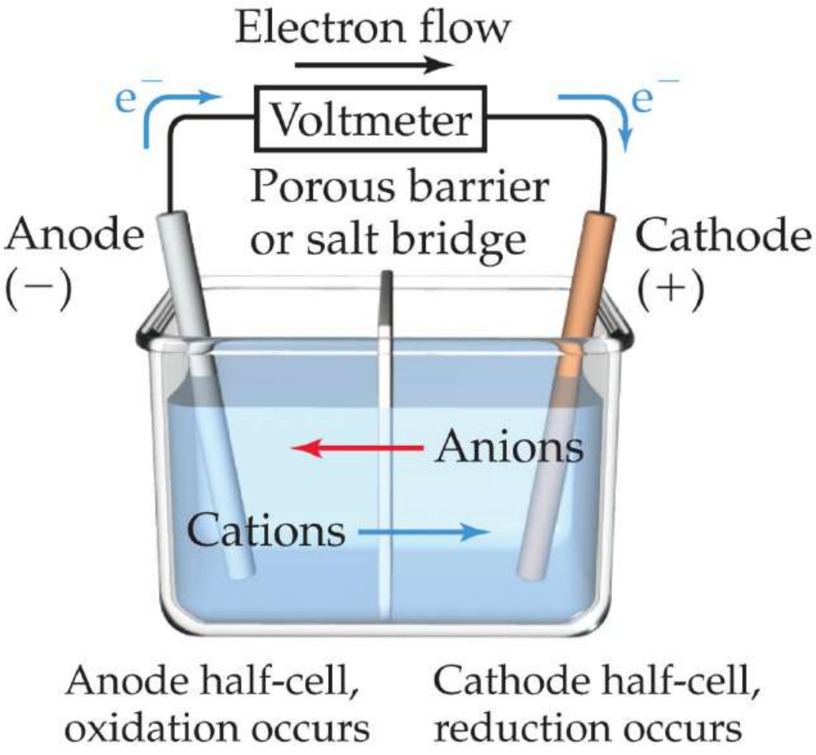


- How is electrical balance maintained in the left beaker as Zn^{2+} is formed at the anode?

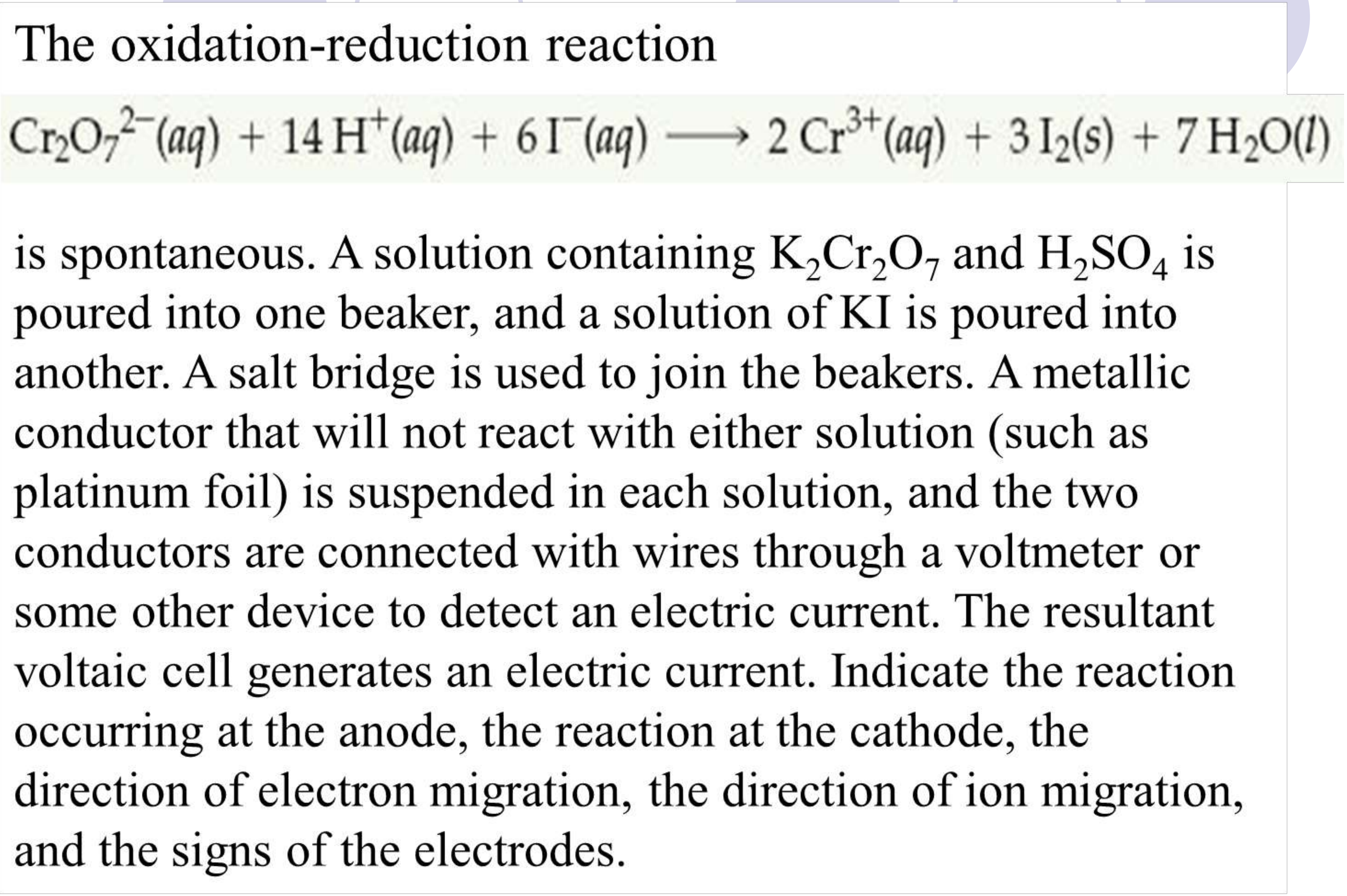


Voltaic Cells

- In the cell, electrons leave the anode and flow through the wire to the cathode.
- Cations are formed in the anode compartment.
- As the electrons reach the cathode, cations in solution are attracted to the now negative cathode.
- The cations gain electrons and are deposited as metal on the cathode.



Sample Exercise 20.4 Describing a Voltaic Cell



The oxidation-reduction reaction

$$Cr_2O_7^{2-}(aq) + 14\,H^+(aq) + 6\,I^-(aq) \longrightarrow 2\,Cr^{3+}(aq) + 3\,I_2(s) + 7\,H_2O(l)$$

is spontaneous. A solution containing $K_2Cr_2O_7$ and H_2SO_4 is poured into one beaker, and a solution of KI is poured into another. A salt bridge is used to join the beakers. A metallic conductor that will not react with either solution (such as platinum foil) is suspended in each solution, and the two conductors are connected with wires through a voltmeter or some other device to detect an electric current. The resultant voltaic cell generates an electric current. Indicate the reaction occurring at the anode, the reaction at the cathode, the direction of electron migration, the direction of ion migration, and the signs of the electrodes.

Practice Exercise 1

The following two half-reactions occur in a voltaic cell:

$\mathrm{Ni}(s) \rightarrow \mathrm{Ni}^{2+}(aq) + 2\,e^{-}$ (electrode = Ni)

$\mathrm{Cu}^{2+}(aq) + 2\,e^{-} \rightarrow \mathrm{Cu}(s)$ (electrode = Cu)

Which one of the following descriptions most accurately describes what is occurring in the half-cell containing the Cu electrode and $\mathrm{Cu}^{2+}(aq)$ solution?

- **(a)**The electrode is losing mass and cations from the salt bridge are flowing into the half-cell.
- **(b)**The electrode is gaining mass and cations from the salt bridge are flowing into the half-cell.
- **(c)**The electrode is losing mass and anions from the salt bridge are flowing into the half-cell.
- **(d)**The electrode is gaining mass and anions from the salt bridge are flowing into the half-cell.

Practice Exercise 2

The two half-reactions in a voltaic cell are

$$\mathrm{Zn}(s) \longrightarrow \mathrm{Zn}^{2+}(aq) + 2\,\mathrm{e}^-$$

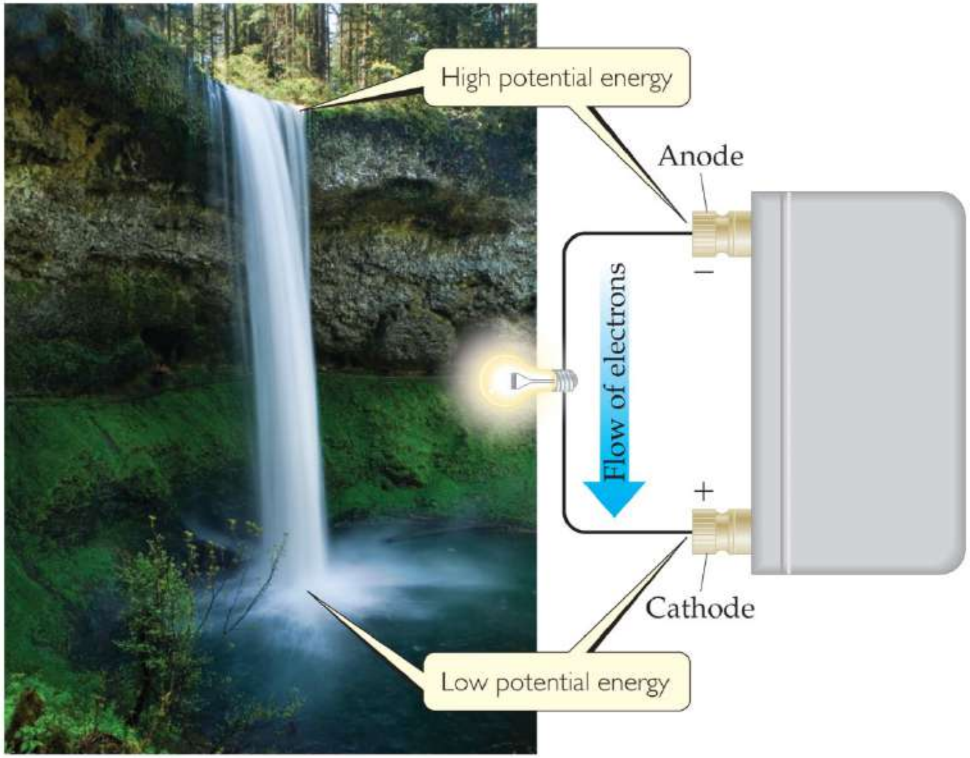
$$\mathrm{ClO_3}^-(aq) + 6\,\mathrm{H}^+(aq) + 6\,\mathrm{e}^- \longrightarrow \mathrm{Cl}^-(aq) + 3\,\mathrm{H_2O}(l)$$

(a) Indicate which reaction occurs at the anode and which at the cathode. **(b)** Does the zinc electrode gain, lose, or retain the same mass as the reaction proceeds? **(c)** Does the platinum electrode gain, lose, or retain the same mass as the reaction proceeds? **(d)** Which electrode is positive?

20.4 Cell Potentials Under Standard Conditions

Electromotive Force (emf)

- Water flows spontaneously one way in a waterfall.
- Comparably, electrons flow spontaneously one way in a redox reaction, from high to low potential energy.



Electromotive Force (emf)

- The potential difference between the anode and cathode in a cell is called the **electromotive force (emf)**.
- It is also called the **cell potential** and is designated E_{cell}.
- It is measured in volts (V). One volt is one joule per coulomb (1 V = 1 J/C).

20.4 Give It Some Thought

- If a standard potential is $E°_{cell}$ = +0.85 V at 25°C, is the redox reaction of the cell spontaneous?

Standard Reduction Potentials

- Reduction potentials for many electrodes have been measured and tabulated.
- The values are compared to the reduction of hydrogen as a standard.

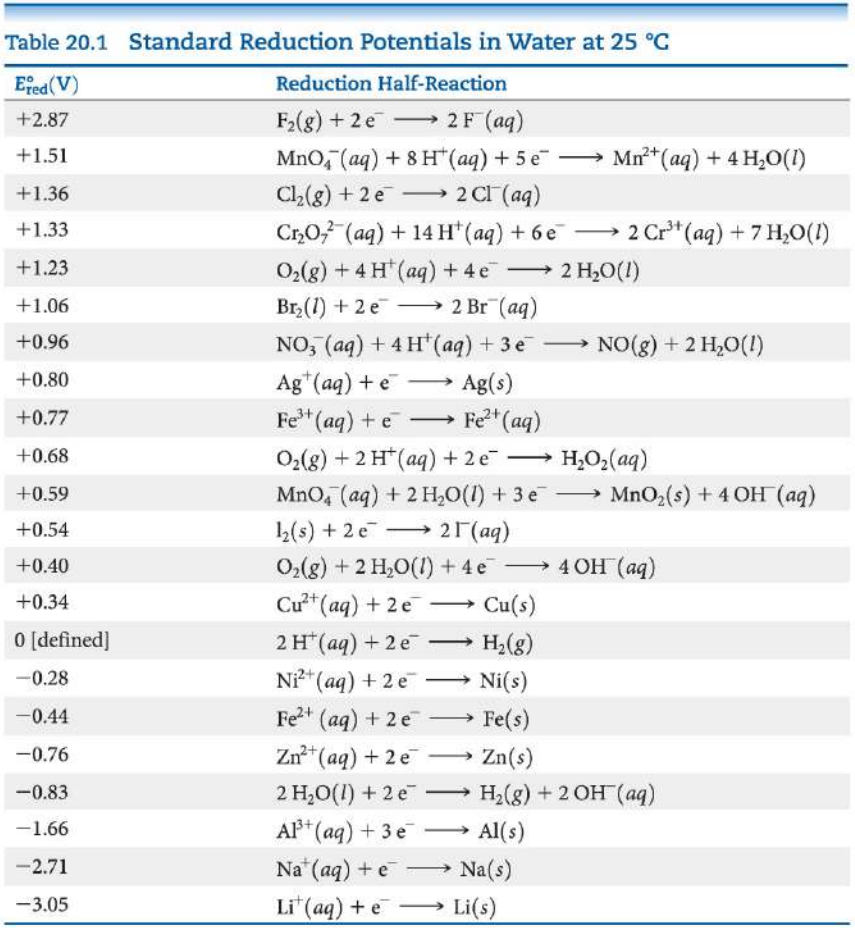
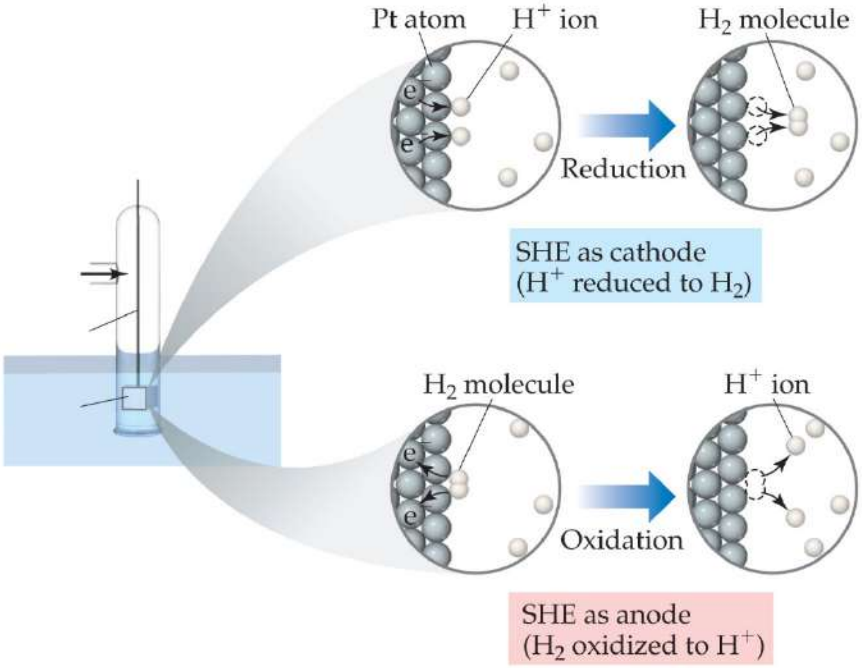


Table 20.1 **Standard Reduction Potentials in Water at 25 °C**

E°_{red}(V)	Reduction Half-Reaction
+2.87	$F_2(g) + 2e^- \longrightarrow 2F^-(aq)$
+1.51	$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$
+1.36	$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$
+1.33	$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$
+1.23	$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)$
+1.06	$Br_2(l) + 2e^- \longrightarrow 2Br^-(aq)$
+0.96	$NO_3^-(aq) + 4H^+(aq) + 3e^- \longrightarrow NO(g) + 2H_2O(l)$
+0.80	$Ag^+(aq) + e^- \longrightarrow Ag(s)$
+0.77	$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$
+0.68	$O_2(g) + 2H^+(aq) + 2e^- \longrightarrow H_2O_2(aq)$
+0.59	$MnO_4^-(aq) + 2H_2O(l) + 3e^- \longrightarrow MnO_2(s) + 4OH^-(aq)$
+0.54	$I_2(s) + 2e^- \longrightarrow 2I^-(aq)$
+0.40	$O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$
+0.34	$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$
0 [defined]	$2H^+(aq) + 2e^- \longrightarrow H_2(g)$
−0.28	$Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$
−0.44	$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$
−0.76	$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$
−0.83	$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$
−1.66	$Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$
−2.71	$Na^+(aq) + e^- \longrightarrow Na(s)$
−3.05	$Li^+(aq) + e^- \longrightarrow Li(s)$

Standard Hydrogen Electrode

- Their reference is called the standard hydrogen electrode (SHE).
- By definition as the standard, the reduction potential for hydrogen is 0 V:



$$2\,H^+_{(aq,\,1M)} + 2e^- \longrightarrow H_{2(g,\,1\text{ atm})}$$

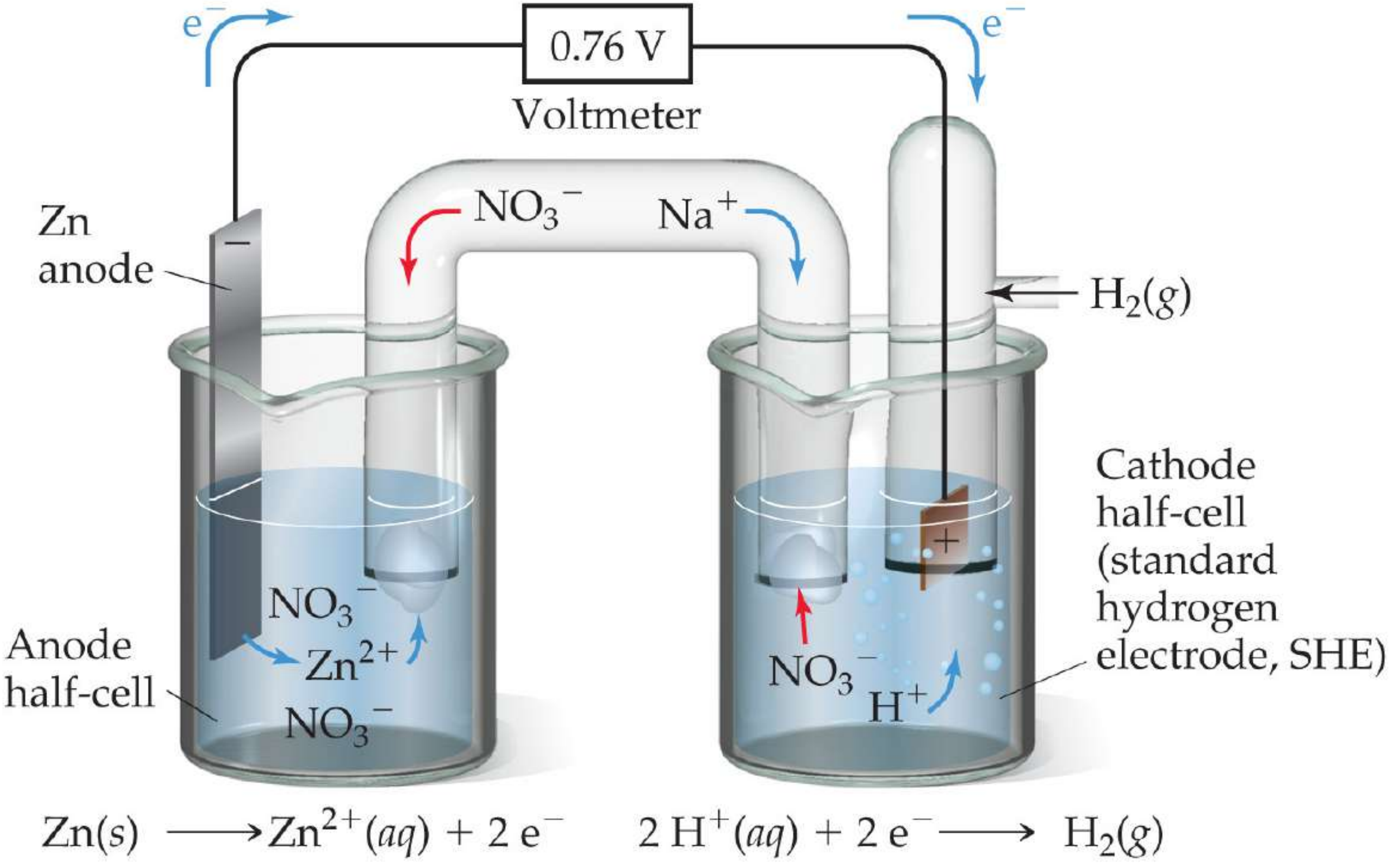
Standard Cell Potentials

The cell potential at standard conditions can be found through this equation:

$$E^\circ_{\text{cell}} = E^\circ_{\text{red}}\text{ (cathode)} - E^\circ_{\text{red}}\text{ (anode)}$$

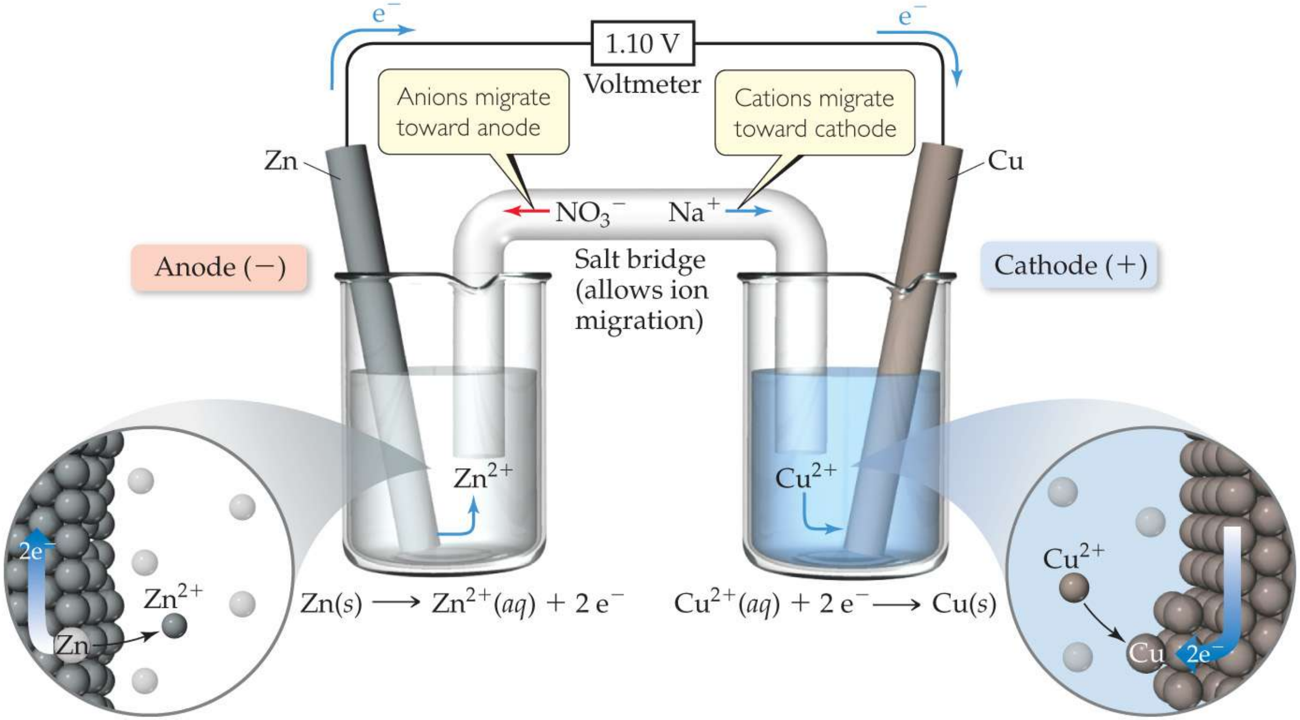
Because cell potential is based on the potential energy per unit of charge, it is an intensive property.

Why do Na^+ ions migrate into the cathode half-cell as the reaction proceeds?



Cell Potentials

- For the anode in this cell, $E°_{red}$ = –0.76 V
- For the cathode, $E°_{red}$ = +0.34 V
- So, for the cell, $E°_{cell}$ = $E°_{red}$ (anode) – $E°_{red}$ (cathode)
  = +0.34 V – (–0.76 V) = +1.10 V



20.4 Give It Some Thought

- For the half-reaction $Cl_2(g) + 2\ e^- \rightarrow 2\ Cl^-(aq)$, what are the standard conditions for the reactant and product?

Sample Exercise 20.5 Calculating E°_{red} from E°_{cell}

For the Zn–Cu^{2+} voltaic cell shown in Figure 20.5, we have

$$\mathrm{Zn}(s) + \mathrm{Cu}^{2+}(aq, 1\,M) \longrightarrow \mathrm{Zn}^{2+}(aq, 1\,M) + \mathrm{Cu}(s) \qquad E^\circ_{cell} = 1.10\ \mathrm{V}$$

Given that the standard reduction potential of Zn^{2+} to $Zn(s)$ is –0.76 V, calculate the E°_{red} for the reduction of Cu^{2+} to Cu:

$$\mathrm{Cu}^{2+}(aq, 1\,M) + 2\,\mathrm{e}^- \longrightarrow \mathrm{Cu}(s)$$

Practice Exercise 1

A voltaic cell based on the reaction 2 $Eu^{2+}(aq)$ + $Ni^{2+}(aq) \rightarrow 2\,Eu^{3+}(aq) + Ni(s)$ generates $E°_{cell}$ = 0.07 V. Given the standard reduction potential of Ni^{2+} given in Table 20.1 what is the standard reduction potential for the reaction $Eu^{3+}(aq) + e^{-} \rightarrow Eu^{2+}(aq)$?

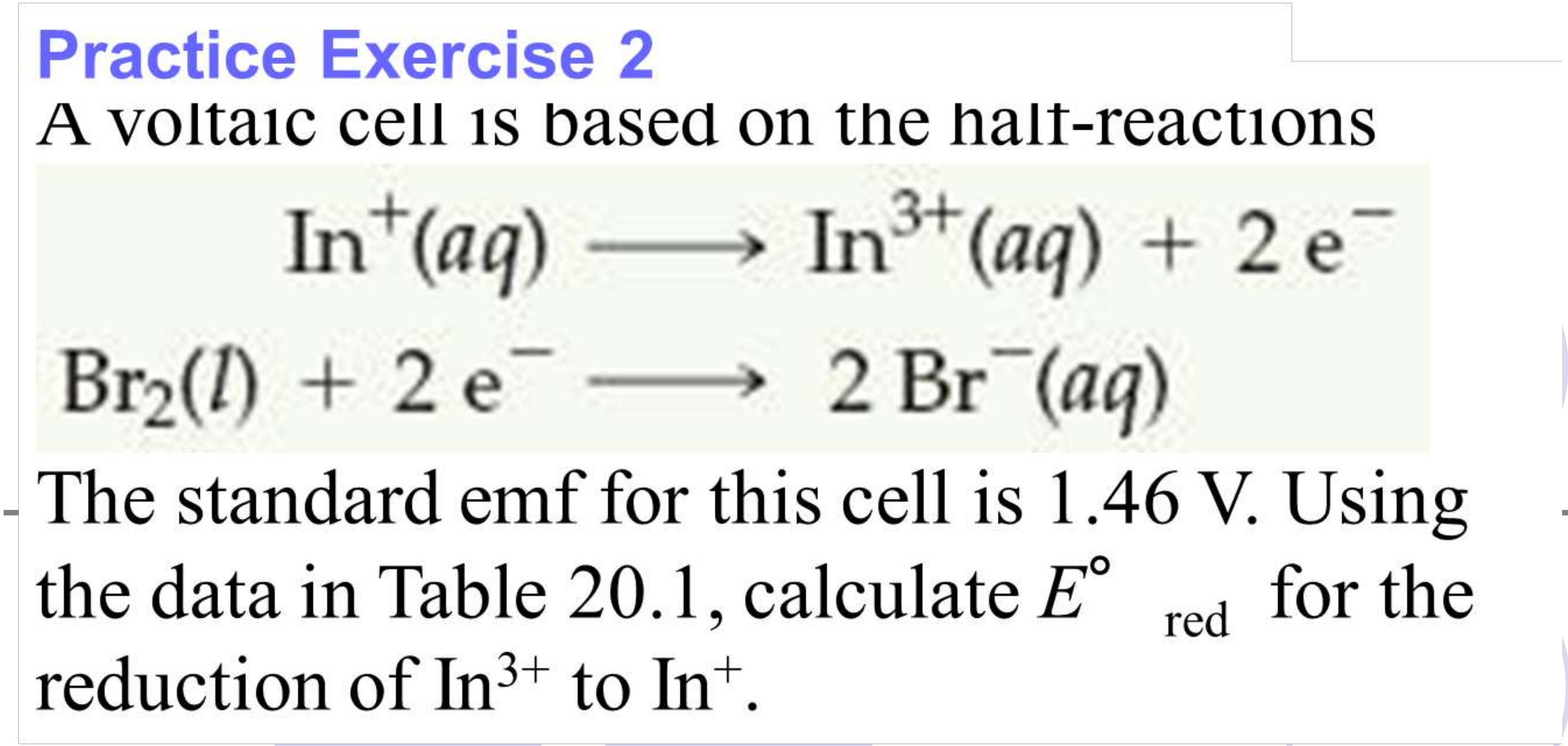
(a) –0.35 V

(b) 0.35 V

(c) –0.21 V

(d) 0.21 V

(e) 0.07 V



Practice Exercise 2

A voltaic cell is based on the half-reactions

$$\mathrm{In^{+}}(aq) \longrightarrow \mathrm{In^{3+}}(aq) + 2\,\mathrm{e^{-}}$$

$$\mathrm{Br_2}(l) + 2\,\mathrm{e^{-}} \longrightarrow 2\,\mathrm{Br^{-}}(aq)$$

The standard emf for this cell is 1.46 V. Using the data in Table 20.1, calculate E°_{red} for the reduction of $\mathrm{In^{3+}}$ to $\mathrm{In^{+}}$.

Sample Exercise 20.6 Calculating E°_{cell} from E°_{red}

Use Table 20.1 to calculate E°cell for the voltaic cell described in Sample Exercise 20.4, which is based on the reaction:

$$Cr_2O_7^{2-}(aq) + 14\,H^{+}(aq) + 6\,I^{-}(aq) \longrightarrow 2\,Cr^{3+}(aq) + 3\,I_2(s) + 7\,H_2O(l)$$

Practice Exercise 1

Using the data in Table 20.1 what value would you calculate for the standard emf ($E°_{cell}$) for a voltaic cell that employs the overall cell reaction $2\ Ag^+(aq) + Ni(s) \rightarrow 2\ Ag(s) + Ni^{2+}(aq)$?

(a) +0.52 V

(b) –0.52 V

(c) +1.08 V

(d) –1.08 V

(e) +0.80 V

Practice Exercise 2

Using data in Table 20.1, calculate the standard emf for a cell that employs the following overall cell reaction:

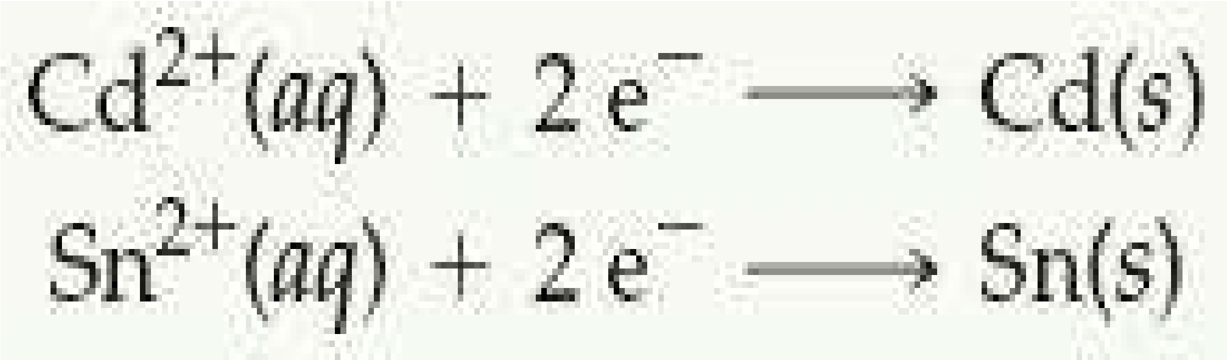
$$2\,\mathrm{Al}(s) + 3\,\mathrm{I_2}(s) \longrightarrow 2\,\mathrm{Al^{3+}}(aq) + 6\,\mathrm{I^-}(aq)$$

20.4 Give It Some Thought

- The standard reduction potential of $Ni^{2+}(aq)$ is $E°_{red}$ = -0.28 V and that $Fe^{2+}(aq)$ is $E°_{red}$ = -0.44 V. In a Ni-Fe voltaic cell, which electrode is the cathode, Ni or Fe?

Sample Exercise 20.7 Determining Half-Reactions at electrodes and Calculating Cell EMF

A voltaic cell is based on the following two standard half-reactions:



$$Cd^{2+}(aq) + 2\,e^- \longrightarrow Cd(s)$$

$$Sn^{2+}(aq) + 2\,e^- \longrightarrow Sn(s)$$

By using the data in Appendix E, determine **(a)** the half-reactions that occur at the cathode and the anode, and **(b)** the standard cell potential.

Practice Exercise 1

Consider three voltaic cells, each similar to the one shown in Figure 20.5. In each voltaic cell, one half-cell contains a 1.0 *M* $Fe(NO_3)_2(aq)$ solution with an Fe electrode. The contents of the other half-cells are as follows:

Cell 1: a 1.0 *M* $CuCl_2(aq)$ solution with a Cu electrode
Cell 2: a 1.0 *M* $NiCl_2(aq)$ solution with a Ni electrode
Cell 3: a 1.0 *M* $ZnCl_2(aq)$ solution with a Zn electrode

In which voltaic cell(s) does iron act as the anode?

(a) Cell 1
(b) Cell 2
(c) Cell 3
(d) Cells 1 and 2
(e) All three cells

Practice Exercise 2

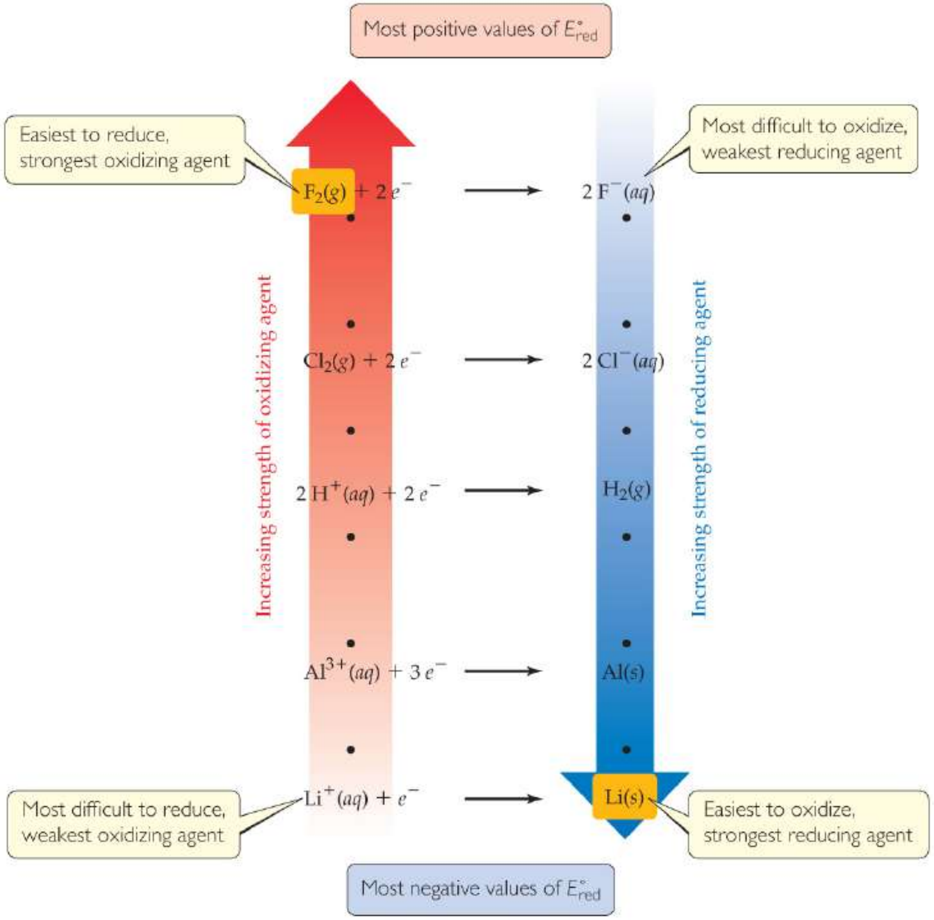
A voltaic cell is based on a Co^{2+}/Co half-cell and an $AgCl/Ag$ half-cell.

(a) What half-reaction occurs at the anode?

(b) What is the standard cell potential?

Oxidizing and Reducing Agents

- The more positive the value of $E°_{red}$, the greater the tendency for reduction under standard conditions.
- The strongest oxidizers have the most positive reduction potentials.
- The strongest reducers have the most negative reduction potentials.



Most positive values of $E°_{red}$

Easiest to reduce, strongest oxidizing agent

Most difficult to oxidize, weakest reducing agent

Most difficult to reduce, weakest oxidizing agent

Easiest to oxidize, strongest reducing agent

Most negative values of $E°_{red}$

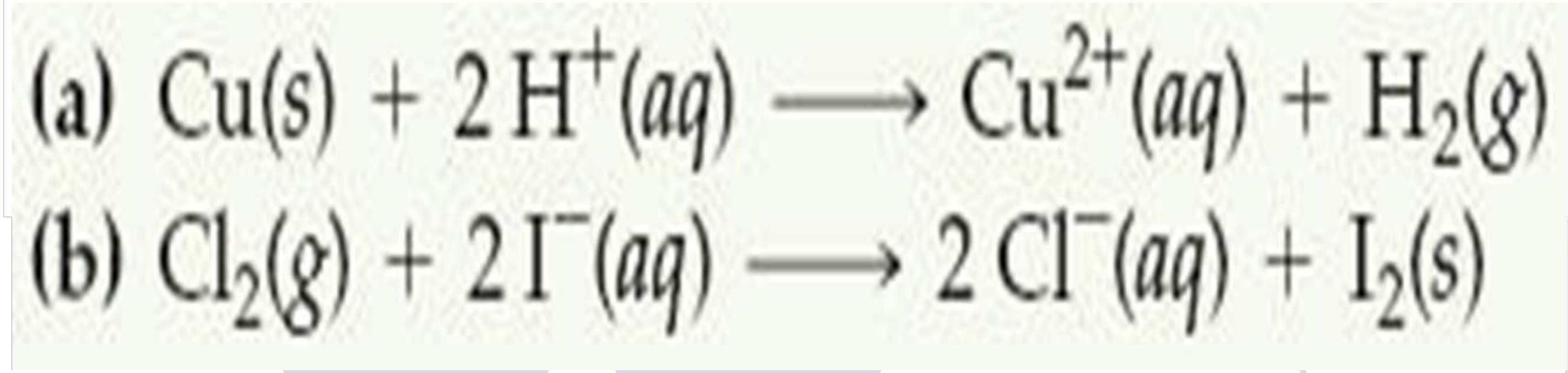
20.5 Free Energy and Redox Reactions

Free Energy and Redox

- Spontaneous redox reactions produce a positive cell potential, or emf.
- $E° = E°_{red}$ (reduction) – $E°_{red}$ (oxidation)
- Note that this is true for ALL redox reactions, not only for voltaic cells.
- Since Gibbs free energy is the measure of spontaneity, positive emf corresponds to negative ΔG.
- How do they relate? $\Delta G = -nFE$ (F is the Faraday constant, 96,485 C/mol.)

Sample Exercise 20.9 Spontaneous or Not?

Using standard reduction potentials in Table 20.1, determine whether the following reactions are spontaneous under standard conditions.

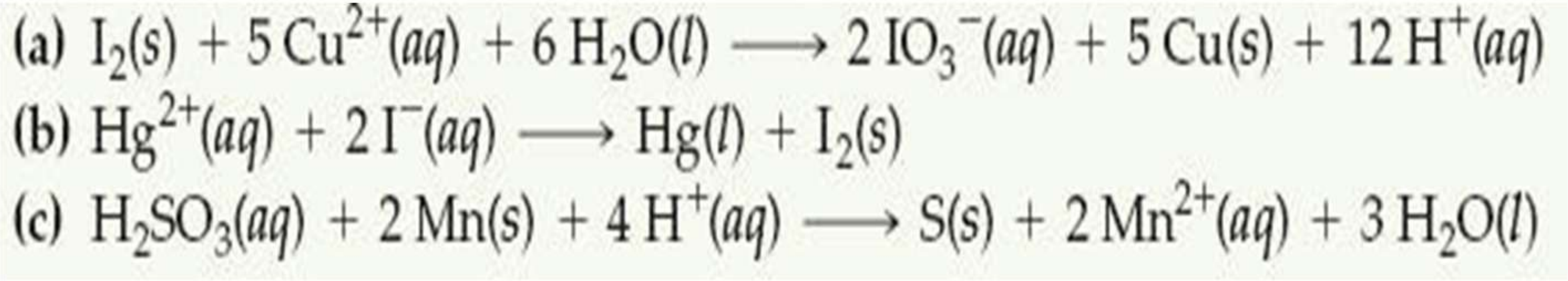


(a) $Cu(s) + 2\,H^{+}(aq) \longrightarrow Cu^{2+}(aq) + H_2(g)$

(b) $Cl_2(g) + 2\,I^{-}(aq) \longrightarrow 2\,Cl^{-}(aq) + I_2(s)$

Practice Exercise 2

Using the standard reduction potentials listed in Appendix E, determine which of the following reactions are spontaneous under standard conditions:



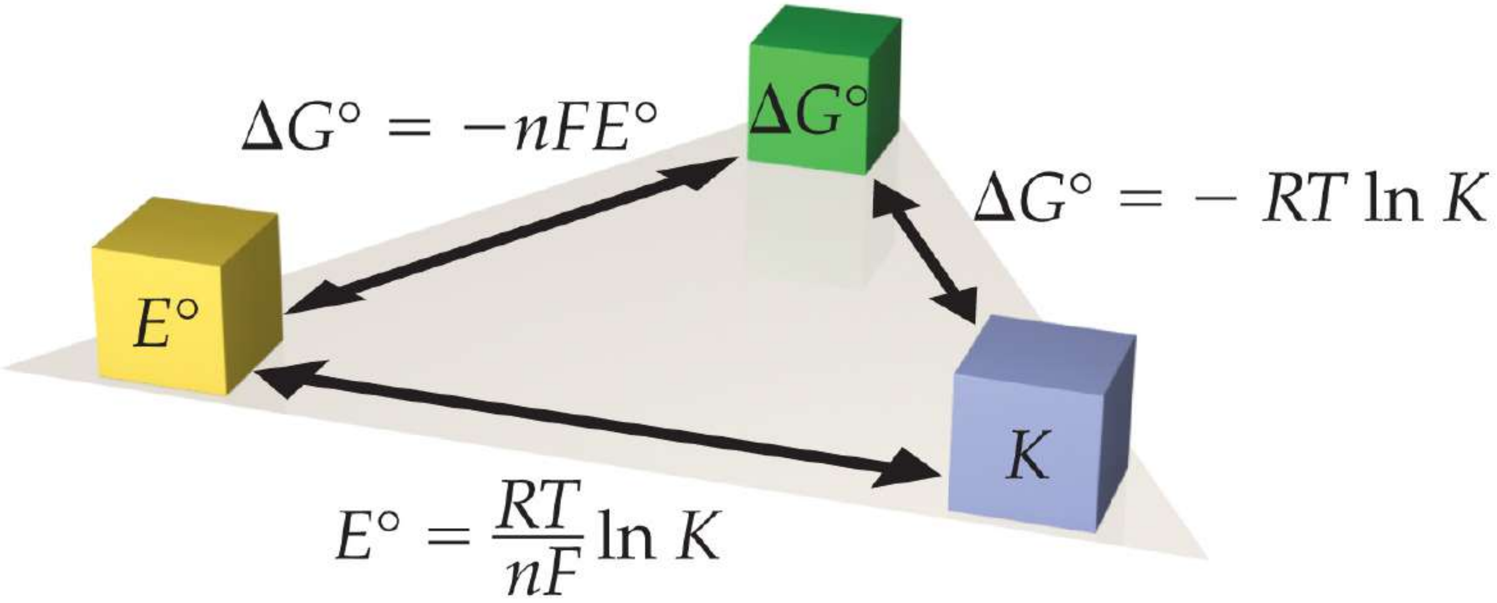
(a) $I_2(s) + 5\,Cu^{2+}(aq) + 6\,H_2O(l) \longrightarrow 2\,IO_3^-(aq) + 5\,Cu(s) + 12\,H^+(aq)$

(b) $Hg^{2+}(aq) + 2\,I^-(aq) \longrightarrow Hg(l) + I_2(s)$

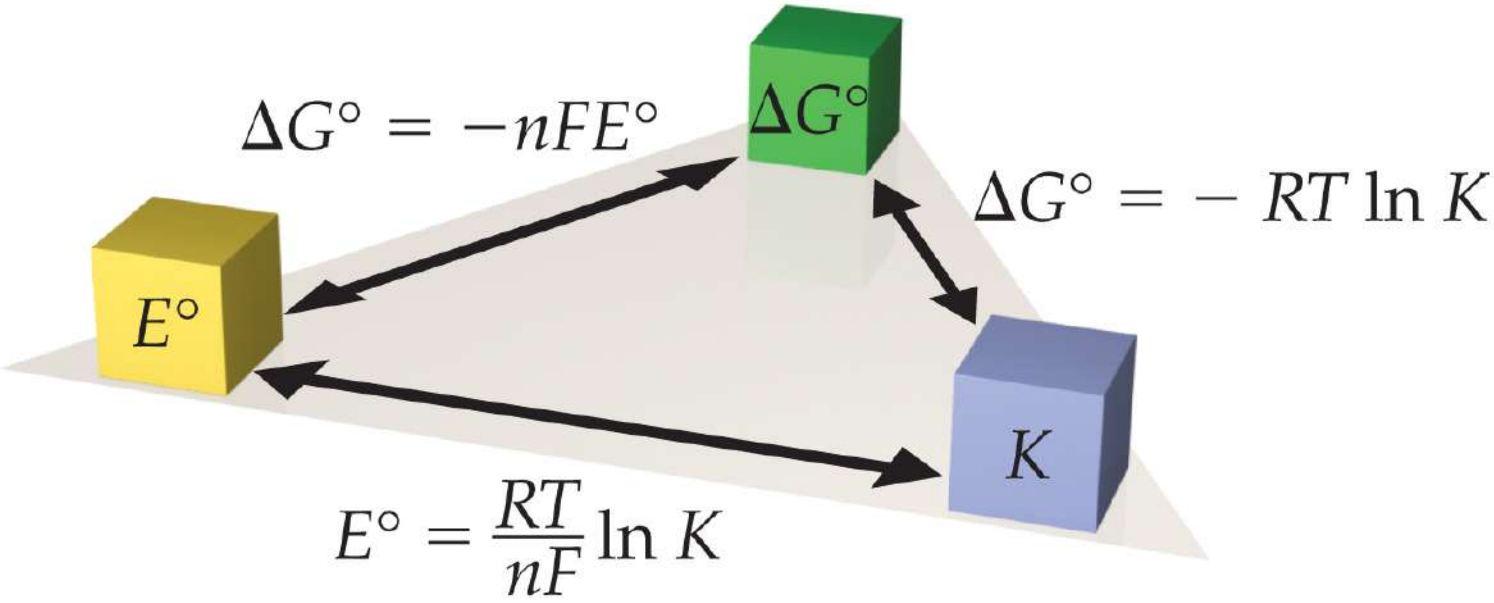
(c) $H_2SO_3(aq) + 2\,Mn(s) + 4\,H^+(aq) \longrightarrow S(s) + 2\,Mn^{2+}(aq) + 3\,H_2O(l)$

Free Energy, Redox, and K

- How is everything related?
- $\Delta G° = -nFE° = -RT \ln K$



What does the variable *n* represent in the ΔG° and *E*° equations?



Sample Exercise 20.10 Determining Δ $G°$ and K

(a) Use the standard reduction potentials listed in Table 20.1 to calculate the standard free-energy change, , and the equilibrium constant, *K*, at 298 K for the reaction

$$4\,\mathrm{Ag}(s) + \mathrm{O_2}(g) + 4\,\mathrm{H^+}(aq) \longrightarrow 4\,\mathrm{Ag^+}(aq) + 2\,\mathrm{H_2O}(l)$$

(b) Suppose the reaction in part (a) was written

$$2\,\mathrm{Ag}(s) + \tfrac{1}{2}\,\mathrm{O_2}(g) + 2\,\mathrm{H^+}(aq) \longrightarrow 2\,\mathrm{Ag^+}(aq) + \mathrm{H_2O}(l)$$

What are the values of $E°$, $\Delta G°$, and *K* when the reaction is written in this way?

Practice Exercise 1

For the reaction

$$3\,\mathrm{Ni}^{2+}(aq) + 2\,\mathrm{Cr(OH)}_3(s) + 10\,\mathrm{OH}^{-}(aq) \rightarrow 3\,\mathrm{Ni}(s) + 2\,\mathrm{CrO}_4^{2-}(aq) + 8\,\mathrm{H}_2\mathrm{O}(l)$$

$\Delta G^\circ = +87$ kJ/mol. Given the standard reduction potential of $\mathrm{Ni}^{2+}(aq)$ in Table 20.1, what value do you calculate for the standard reduction potential of the half-reaction $\mathrm{CrO}_4^{2-}(aq) + 4\,\mathrm{H}_2\mathrm{O}(l) + 3\,e^{-} \rightarrow \mathrm{Cr(OH)}_3(s) + 5\,\mathrm{OH}^{-}(aq)$?

(a) –0.43 V

(b) –0.28 V

(c) 0.02 V

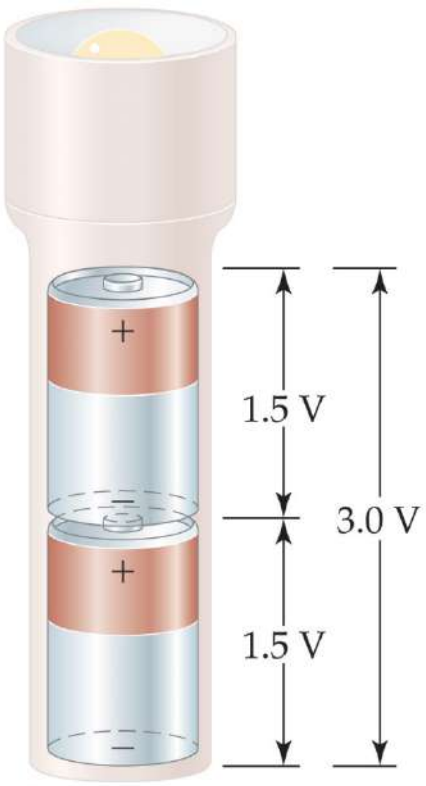
(d) –0.13 V

(e) –0.15 V

20.7 Batteries and Fuel Cells

Some Applications of Cells

- Electrochemistry can be applied as follows:
- Batteries: a portable, self-contained electrochemical power source that consists of one or more voltaic cells.
  - Batteries can be primary cells (cannot be recharged when "dead"—the reaction is complete) or secondary cells (can be recharged).
- Prevention of corrosion ("rust-proofing")
- Electrolysis

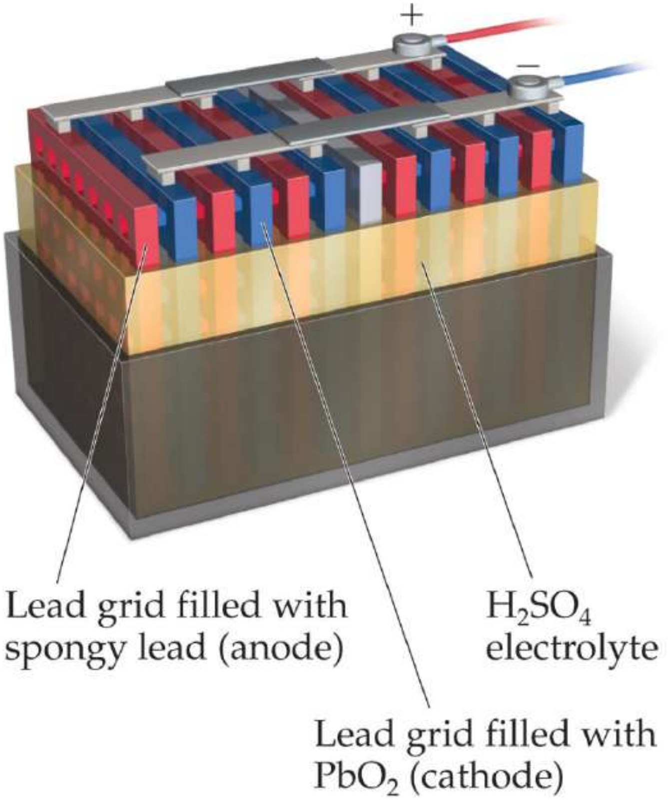


Some Examples of Batteries

- Lead–acid battery: reactants and products are solids, so Q is 1 and the potential is independent of concentrations; however, made with lead and sulfuric acid (hazards).
- Alkaline battery: most common primary battery.
- Ni–Cd and Ni–metal hydride batteries: lightweight, rechargeable; Cd is toxic and heavy, so hydrides are replacing it.
- Lithium-ion batteries: rechargeable, light; produce more voltage than Ni-based batteries.

Some Batteries

Lead–Acid Battery

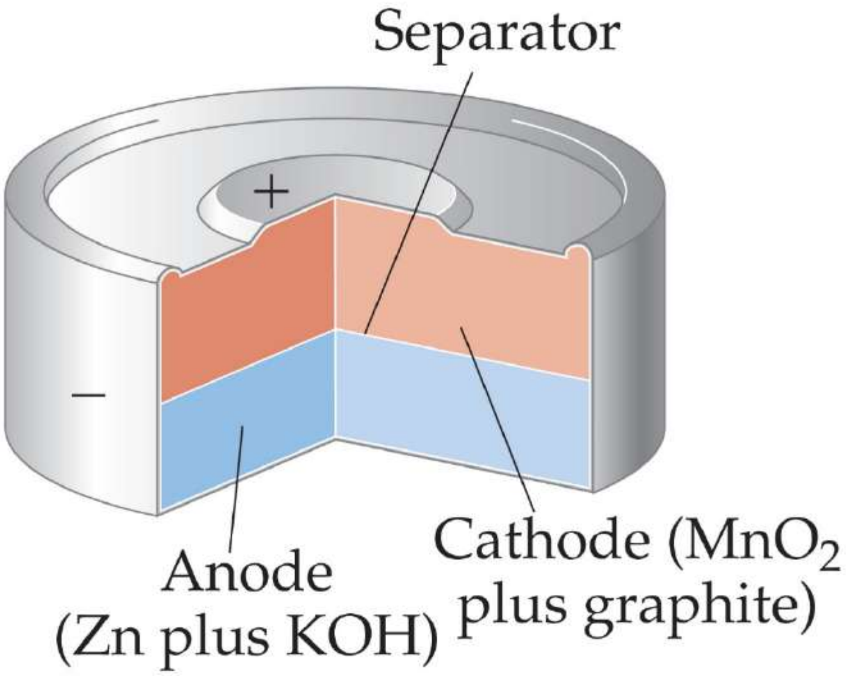


What is the oxidation state of lead in the cathode of this battery?

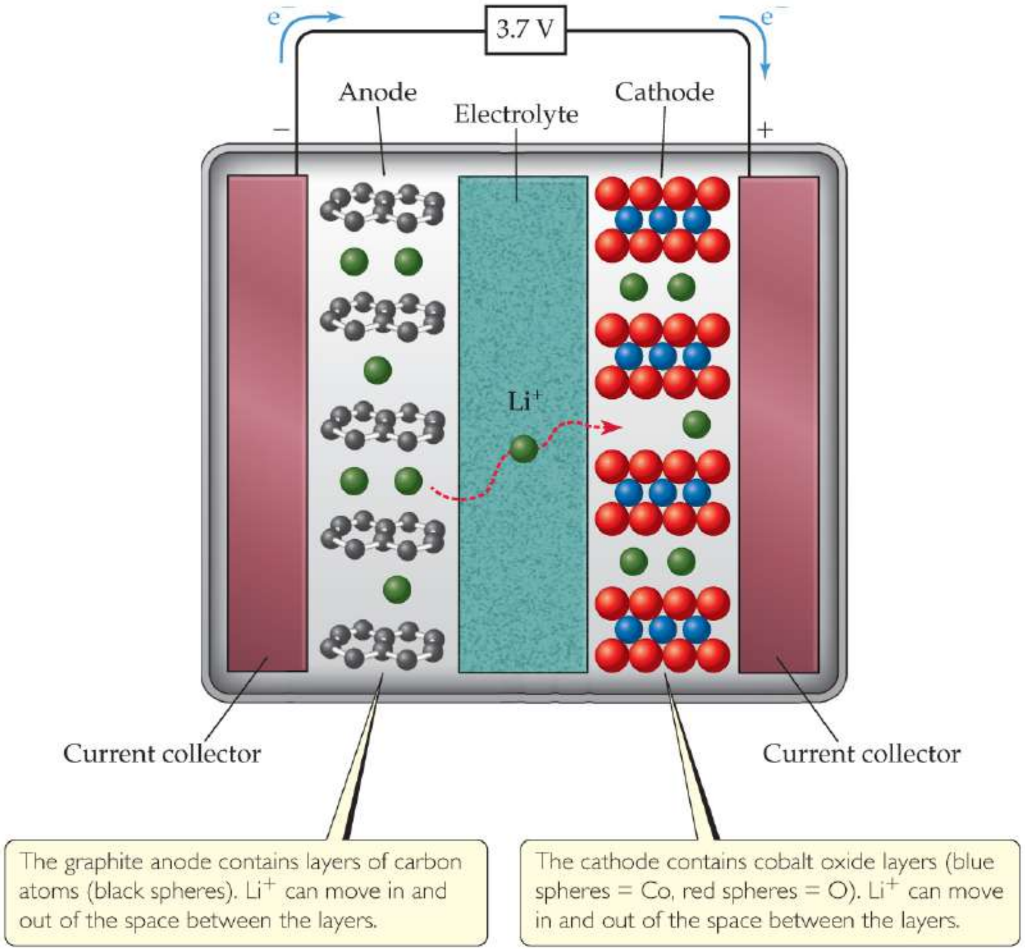
Some Batteries

What substance is oxidized as the battery discharges?

Alkaline Battery



When a Li-ion battery is fully discharged, the cathode has an empirical formula of $LiCoO_2$. What is the oxidation number of cobalt in this state? Does the oxidation numb er of cobalt increase or decrease as the battery charges?



The graphite anode contains layers of carbon atoms (black spheres). Li^+ can move in and out of the space between the layers.

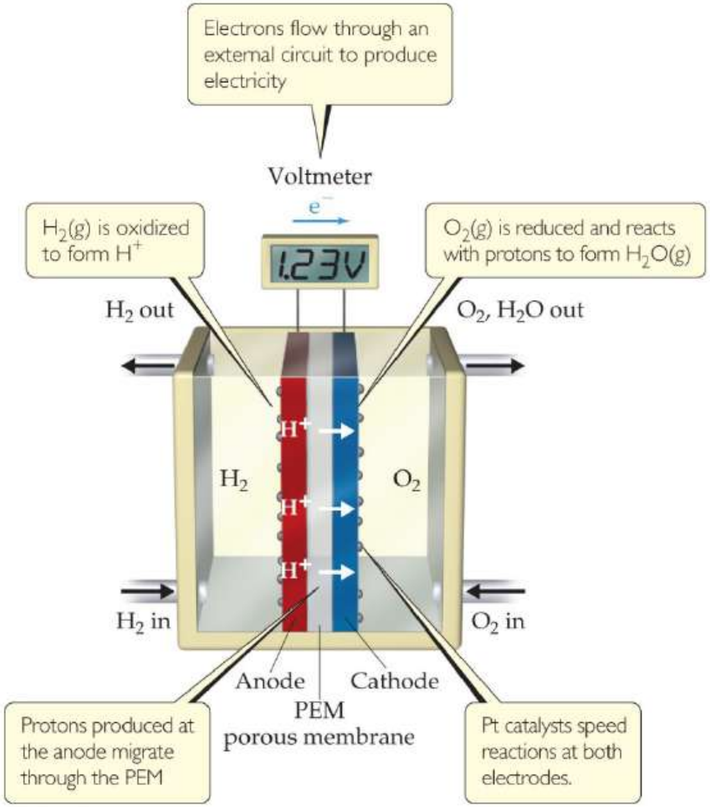
The cathode contains cobalt oxide layers (blue spheres = Co, red spheres = O). Li^+ can move in and out of the space between the layers.

Fuel Cells

- When a fuel is burned, the energy created can be converted to electrical energy.
- Usually, this conversion is only 40% efficient, with the remainder lost as heat.
- The direct conversion of chemical to electrical energy is expected to be more efficient and is the basis for **fuel cells**.
- Fuel cells are NOT batteries; the source of energy must be continuously provided.

Hydrogen Fuel Cells

- In this cell, hydrogen and oxygen form water.
- The cells are twice as efficient as combustion.
- The cells use hydrogen gas as the fuel and oxygen from the air.



Electrons flow through an external circuit to produce electricity

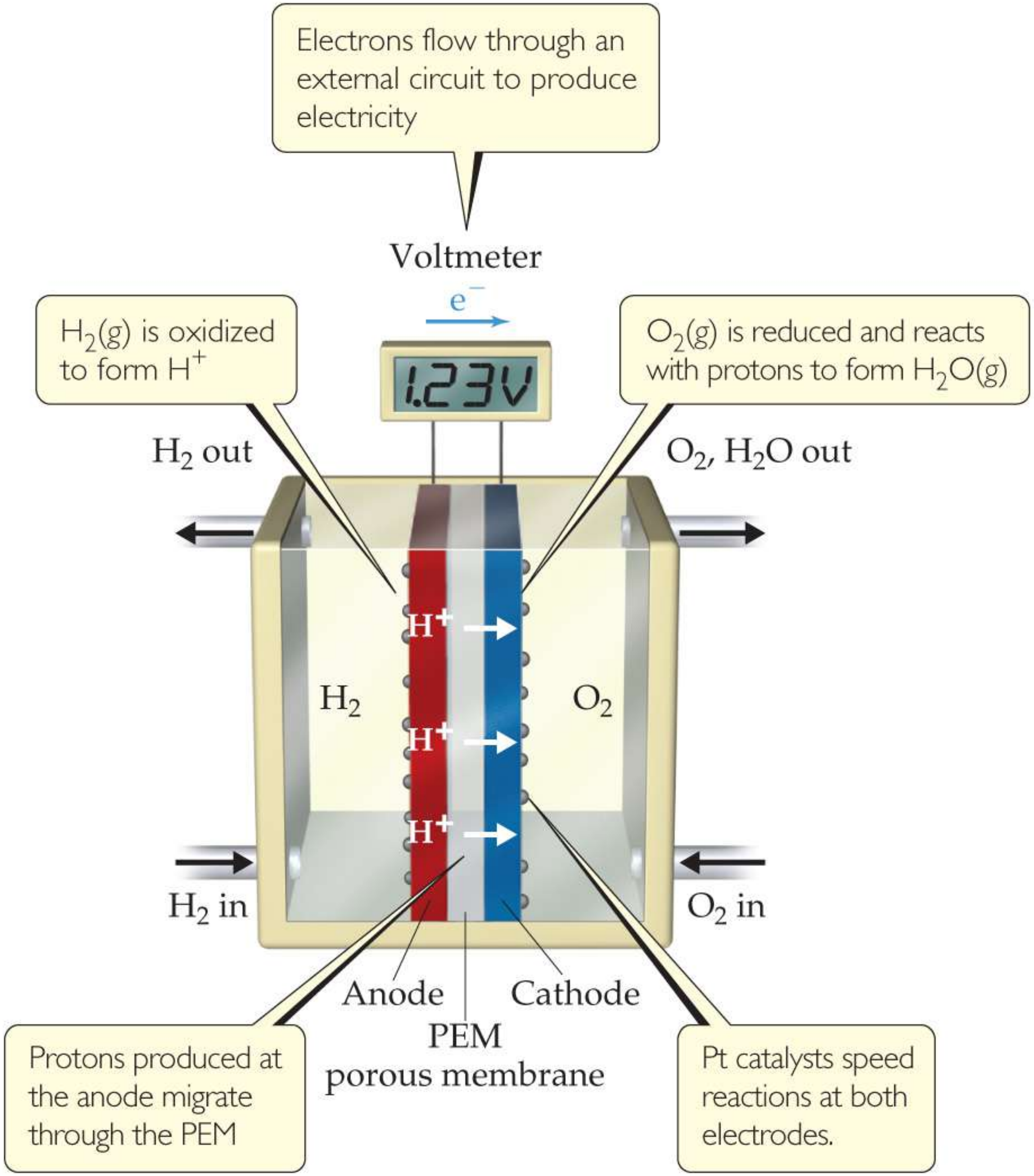
$H_2(g)$ is oxidized to form H^+

$O_2(g)$ is reduced and reacts with protons to form $H_2O(g)$

Protons produced at the anode migrate through the PEM

Pt catalysts speed reactions at both electrodes.

- What half-reaction occurs at the cathode?



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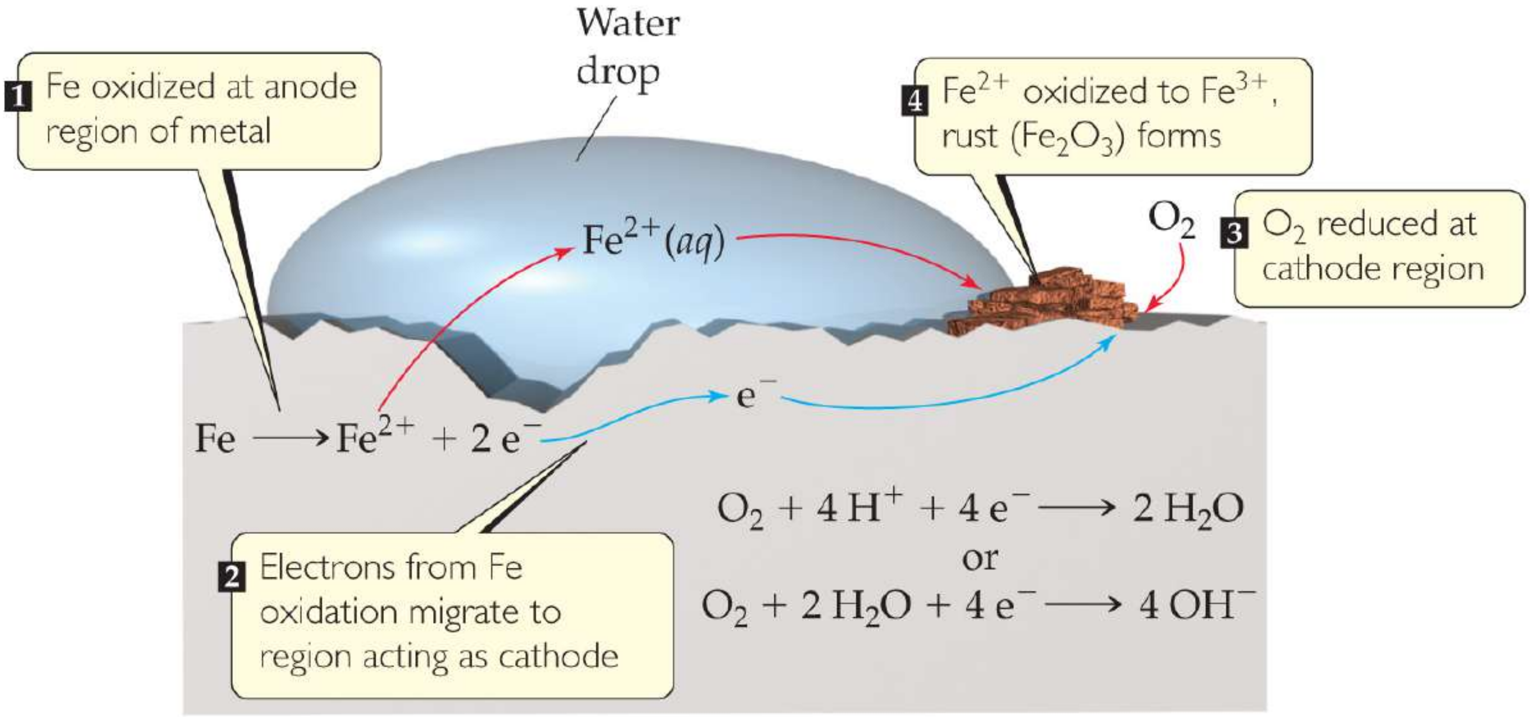
20.8 Corrosion

Corrosion



Water drop

1 Fe oxidized at anode region of metal

2 Electrons from Fe oxidation migrate to region acting as cathode

3 O_2 reduced at cathode region

4 Fe^{2+} oxidized to Fe^{3+}, rust (Fe_2O_3) forms

$$Fe \longrightarrow Fe^{2+} + 2\,e^-$$

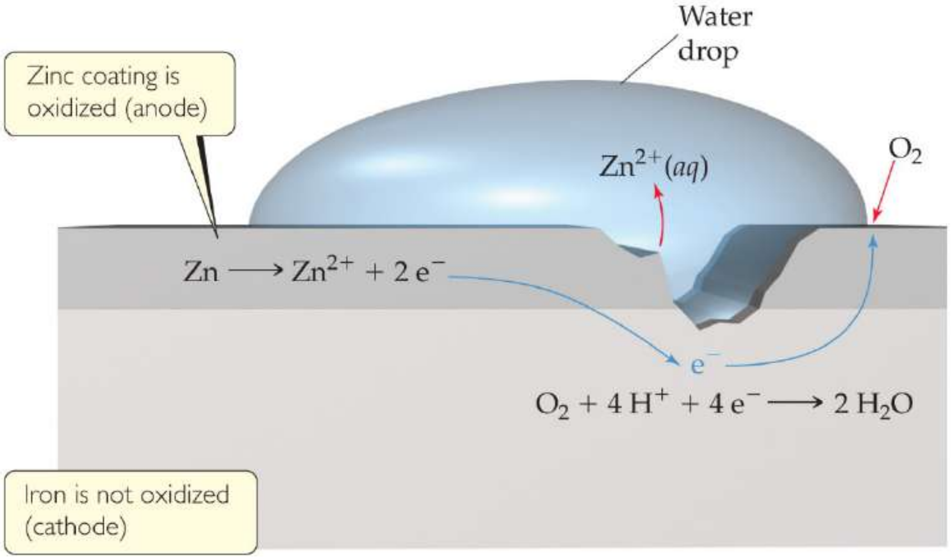
$$O_2 + 4\,H^+ + 4\,e^- \longrightarrow 2\,H_2O$$

or

$$O_2 + 2\,H_2O + 4\,e^- \longrightarrow 4\,OH^-$$

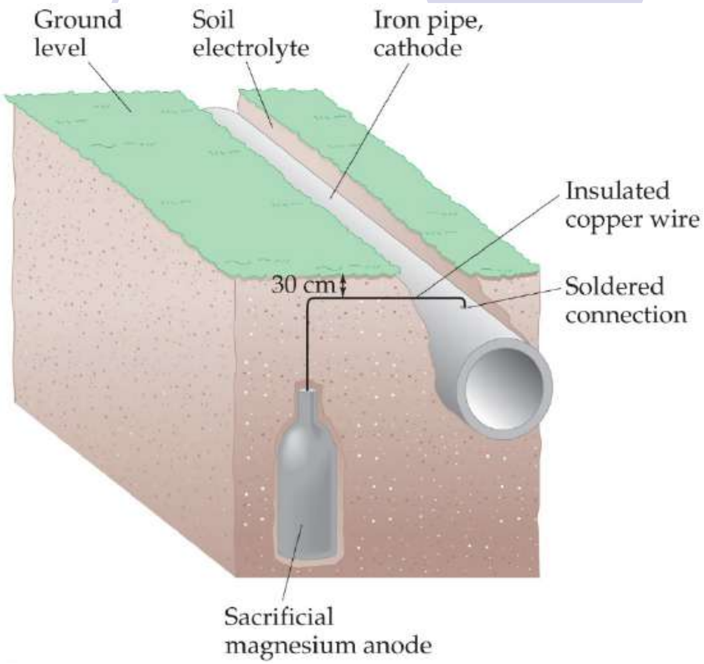
- Corrosion is oxidation.
- Its common name is *rusting*.

Preventing Corrosion



- Corrosion is prevented by coating iron with a metal that is more readily oxidized.
- **Cathodic protection** occurs when zinc is more easily oxidized, so that metal is sacrificed to keep the iron from rusting.

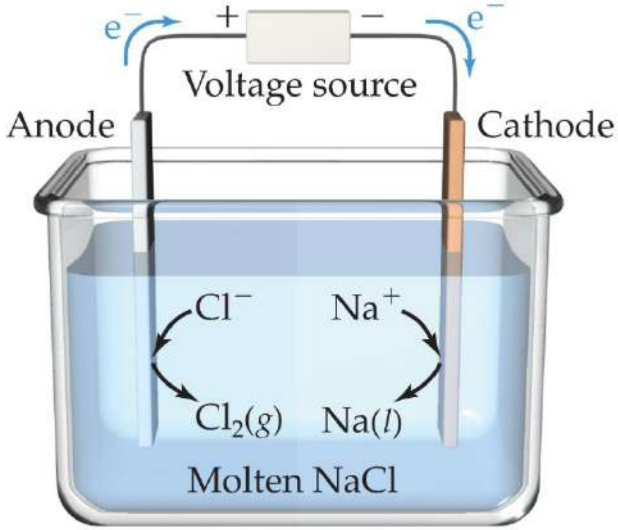
Preventing Corrosion



- Another method to prevent corrosion is used for underground pipes.
- A **sacrificial anode** is attached to the pipe. The anode is oxidized before the pipe.

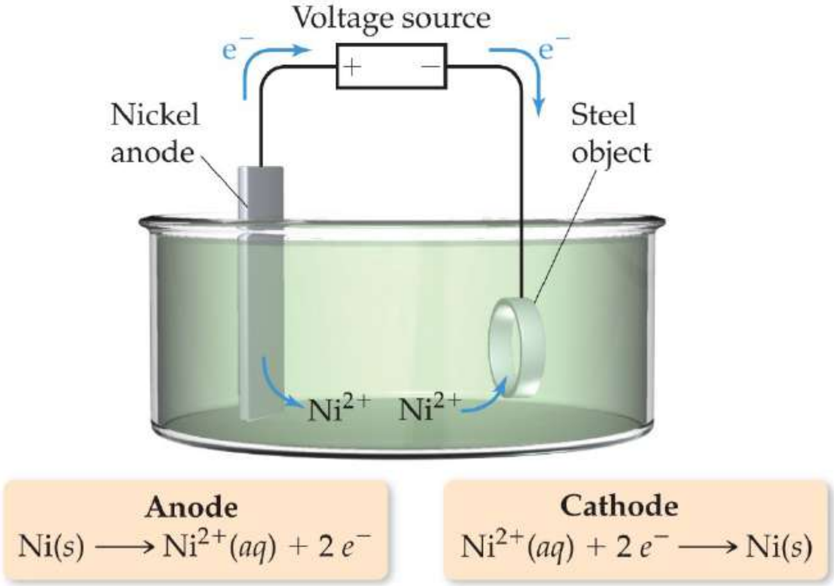
20.9 Electolysis

Electrolysis



$$2\,Cl^- \longrightarrow Cl_2(g) + 2\,e^-$$

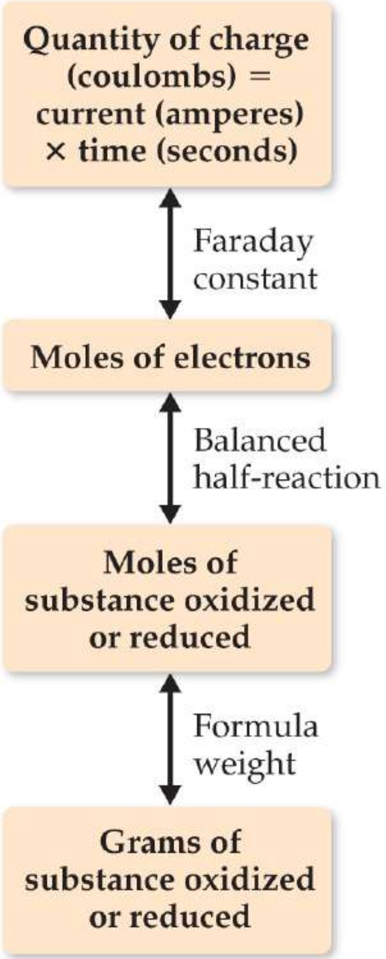
$$2\,Na^+ + 2\,e^- \longrightarrow 2\,Na(l)$$



- Nonspontaneous reactions can occur in electrochemistry IF outside electricity is used to drive the reaction.
- Use of electrical energy to create chemical reactions is called **electrolysis**.

Electrolysis and "Stoichiometry"

- 1 coulomb = 1 ampere × 1 second
- $Q = It = nF$
- Q = charge (C)
- I = current (A)
- t = time (s)
- n = moles of electrons that travel through the wire in the given time
- F = Faraday's constant
- NOTE: n is different than that for the Nernst equation!



Quantity of charge (coulombs) = current (amperes) × time (seconds)

Faraday constant

Moles of electrons

Balanced half-reaction

Moles of substance oxidized or reduced

Formula weight

Grams of substance oxidized or reduced

Sample Exercise 20.14 Relating Electrical Charge and Quantity of Electrolysis

Calculate the number of grams of aluminum produced in 1.00 h by the electrolysis of molten $AlCl_3$ if the electrical current is 10.0 A.

Practice Exercise 1

How much time is needed to deposit 1.0 g of chromium metal from an aqueous solution of $CrCl_3$ using a current of 1.5 A?

(a) 3.8×10^{-2} s

(b) 21 min

(c) 62 min

(d) 139 min

(e) 3.2×10^{3} min

Practice Exercise 2

(a) The half-reaction for formation of magnesium metal upon electrolysis of molten $MgCl_2$ is $Mg^{2+} + 2\,e^- \rightarrow Mg$. Calculate the mass of magnesium formed upon passage of a current of 60.0 A for a period of 4.00×10^3 s.

(b) How many seconds would be required to produce 50.0 g of Mg from $MgCl_2$ if the current is 100.0 A?

Sample Integrative Exercise Putting Concepts Together

The K_{sp} at 298 K for iron(II) fluoride is 2.4×10^{-6}.

(a) Write a half-reaction that gives the likely products of the two-electron reduction of $FeF_2(s)$ in water.

(b) Use the K_{sp} value and the standard reduction potential of $Fe^{2+}(aq)$ to calculate the standard reduction potential for the half-reaction in part (a).

(c) Rationalize the difference in the reduction potential for the half-reaction in part (a) with that for $Fe^{2+}(aq)$.